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Auspices Statement

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Accelerated Carbonate Dissolution as a CO₂ Separation and Sequestration Strategy

By K.G. Caldeira, K.G. Knauss, G.H. Rau

Introduction

We have proposed a technique that could reduce CO₂ emissions from near coastal fossil-fuel power plants using existing power plant cooling water flow rates (Rau and Caldeira, 1999; Caldeira and Rau, 2000). Preliminary cost estimates are as low as \$68 per tonne C sequestered, as compared to > \$170 per tonne C estimated for other approaches to CO₂ separation with geologic or deep-ocean storage. Engineers at McDermott Technologies, Inc., have independently estimated the cost of our proposed technique, and came to the conclusion that our cost estimates were at the high end of the likely range. Interest has been expressed in pursuing this approach further both in Norway and in Japan.

We have proved the viability of our concept using (i) bench-top laboratory experiments (Figures 1 and 2), (ii) computer modeling of those experiments, (iii) more sophisticated cost estimates, and (iv) three-dimensional computer modeling of the consequences to global ocean chemistry (Figure 3 and 4).

The climate and environmental impacts of our current, carbon-intensive energy usage demands that effective and practical energy alternatives and CO₂ mitigation strategies be found. As part of this effort, various means of capturing and storing CO₂ generated from fossil-fuel-based energy production are being investigated (e.g. [3,4]). One of the proposed methods involves a geochemistry-based capture and sequestration process [5,6] that hydrates point-source, waste CO₂ with water to produce a carbonic acid solution. This in turn is reacted and neutralized with limestone, thus converting the

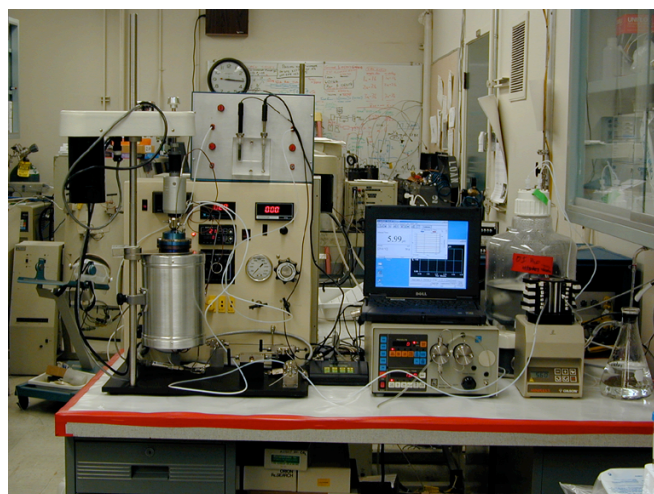
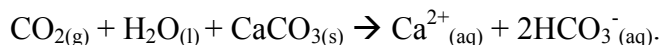


Figure 1. The experimental apparatus described in the text. Limestone dissolution occurs in the metallic cylinder to the left. To the right is data logging and CO₂ equilibration in water.

original CO₂ gas to calcium bicarbonate in solution, the overall reaction being:

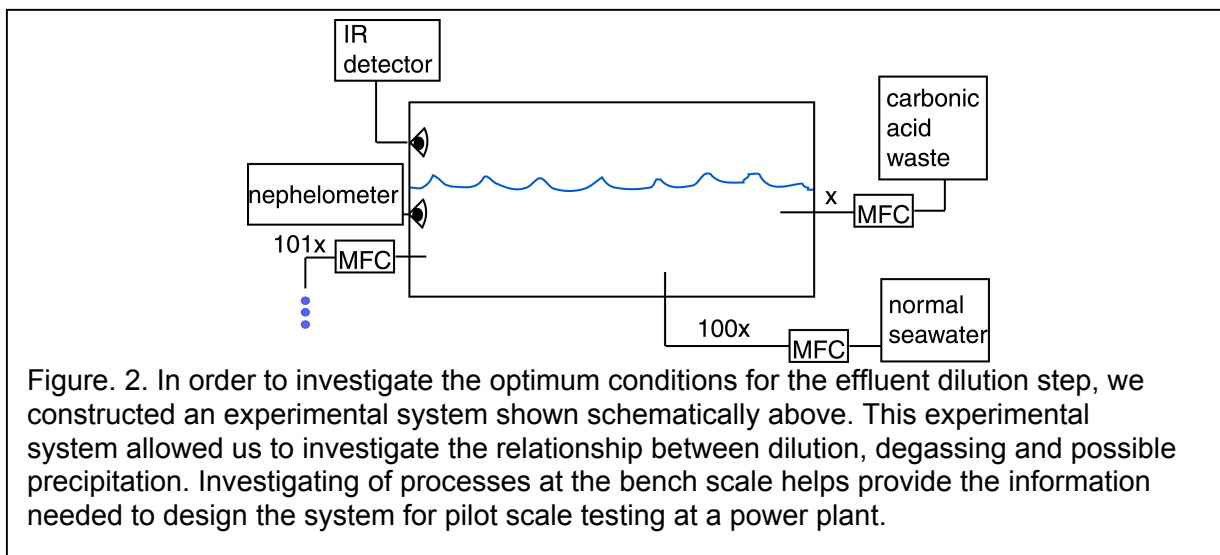


The dissolved calcium bicarbonate produced is then released and diluted in the ocean where it would add minimally to the large, benign pool of these ions already present in seawater.

Such a process is geochemically equivalent to continental and marine carbonate weathering which will otherwise naturally consume anthropogenic CO₂, but over many millennia (e.g. [7,8,9]). We identify the enhanced form of this process as Accelerated Weathering of Limestone or accelerated carbonate dissolution. Previously, it has been shown that accelerated carbonate dissolution can effectively convert a significant fraction of US CO₂ emissions to long-term storage as bicarbonate in the ocean, while avoiding or possibly reversing environmental impacts associated with either the ongoing passive or the proposed active injection of CO₂ into the ocean [6,10]. Being analogous to the widespread use of wet limestone to desulfurize flue gas, accelerated carbonate dissolution reactors could be retrofitted to many existing coastal power plants at a typical cost estimated to be \$20-\$30/tonne CO₂ mitigated [5,11]. This paper further explores limestone availability, cost, transportation, and reaction kinetics as well as ocean and environmental impacts, and the overall economics and practicality of accelerated carbonate dissolution CO₂ mitigation.

Limestone and Seawater Availability

Because the global abundance of water (i.e., seawater) and carbonate is orders of magnitude larger than the entire global reservoir of fossil fuels [12], all anthropogenic emissions of CO₂ could theoretically be mitigated by reaction 1. Indeed, over geologic time scales significant, natural increases in atmospheric CO₂ have been moderated and consumed via carbonate weathering, and the same process will eventually consume the majority of anthropogenic CO₂ as well [7,8]. But if we wait for nature to perform this task, the earth in the meantime would be subjected to much higher atmospheric CO₂ than at present, and for many thousands of years. Thus it is worth considering proactively



speeding up the carbonate weathering process. If the employment of reaction 1 to reduce CO₂ emissions is then not in principle reactant-limited, what are the practical limitations to accelerated carbonate dissolution as a CO₂ capture and sequestration tool?

Based on reaction 1, it would take 2.3 tonnes of calcium carbonate and 0.3 tonnes of water to react 1 tonne of CO₂ to form 2.8 tonnes of HCO₃⁻ in solution. While pure CaCO₃ (calcite and aragonite) is mined and commercially available, its relatively low abundance in this form and its high cost prohibit its use on the scale considered here. Rather it is envisioned that much more abundant and inexpensive limestone (containing 92-98% CaCO₃) would be used. US production of this mineral is presently 10⁹ tonnes/yr [13], and while there are no figures available on the size of the US limestone reserve, it is reasonable to assume that it is sufficient to satisfy current US demand for many decades if not centuries. Channeling the entire yearly US limestone production to accelerated carbonate dissolution could consume roughly 18% of the annual CO₂ generated by electricity production in the US. This implies that a substantial increase in the US

limestone mining rate or foreign importation would be required to accommodate the US demands of both extensive accelerated carbonate dissolution and conventional limestone uses.

There is an important caveat to the preceding conclusion in that currently more than 20% of US limestone production and processing results in waste limestone fines (<10 mm) that have little or no market value and are accumulating at limestone mining and processing sites [14,15]. This suggests that a sizeable, free or low-cost source of limestone could be available for accelerated carbonate dissolution whose use could also help alleviate the significant limestone waste problem.

But even if a free source

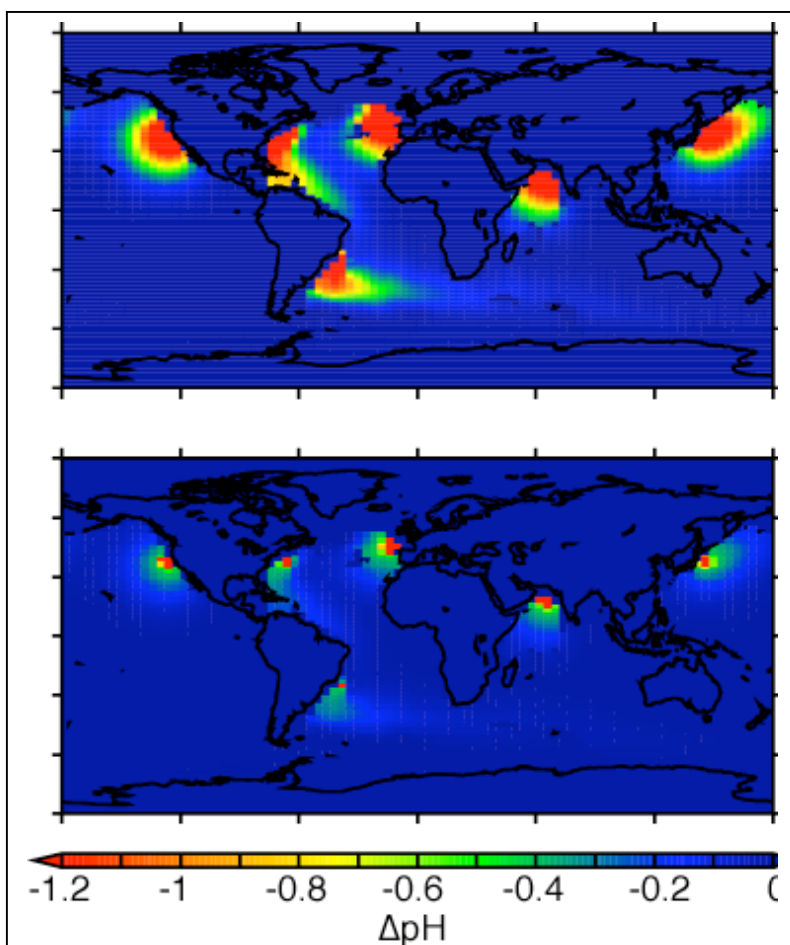


Figure 3. Simulation of pH effects of direct CO₂ injection (top) and the carbonate-dissolution method (bottom). pH effects from carbonate dissolution are 27% that of direct injection, and this could be improved with optimization of engineering parameters investigated experimentally.

of limestone was available, it has been recognized that the cost of transporting such limestone to accelerated carbonate dissolution reactors is a critical factor in the overall economics of the process [5,11]. Also, because of the significant quantities of water required to react the CO_2 and to carry and dilute the resulting bicarbonate ($>10^4$ tonnes $\text{H}_2\text{O}/\text{tonne CO}_2$ [5]), accelerated carbonate dissolution reactors in close proximity to seawater would be at a distinct cost advantage. Even with this geographic limitation, about 12% of CO_2 emissions from US electricity production occurs at plants within 10 km of the US coastline [11]. Fortuitously, the majority of this coastline is also within 400 km of known limestone reserves [16]. This is especially true of the southern and eastern seaboard, which also have the highest density of coastal US power plants and coastal electricity-related CO_2 production. For example there is more than 20 GW of fossil-fueled power generation (≈ 100 billion tonnes CO_2 emitted/yr) by coastal power plants in Florida [11], a state that essentially is entirely underlain by carbonate deposits [17]. In such ideal settings, if both limestone and its transportation costs were negligible, the CO_2

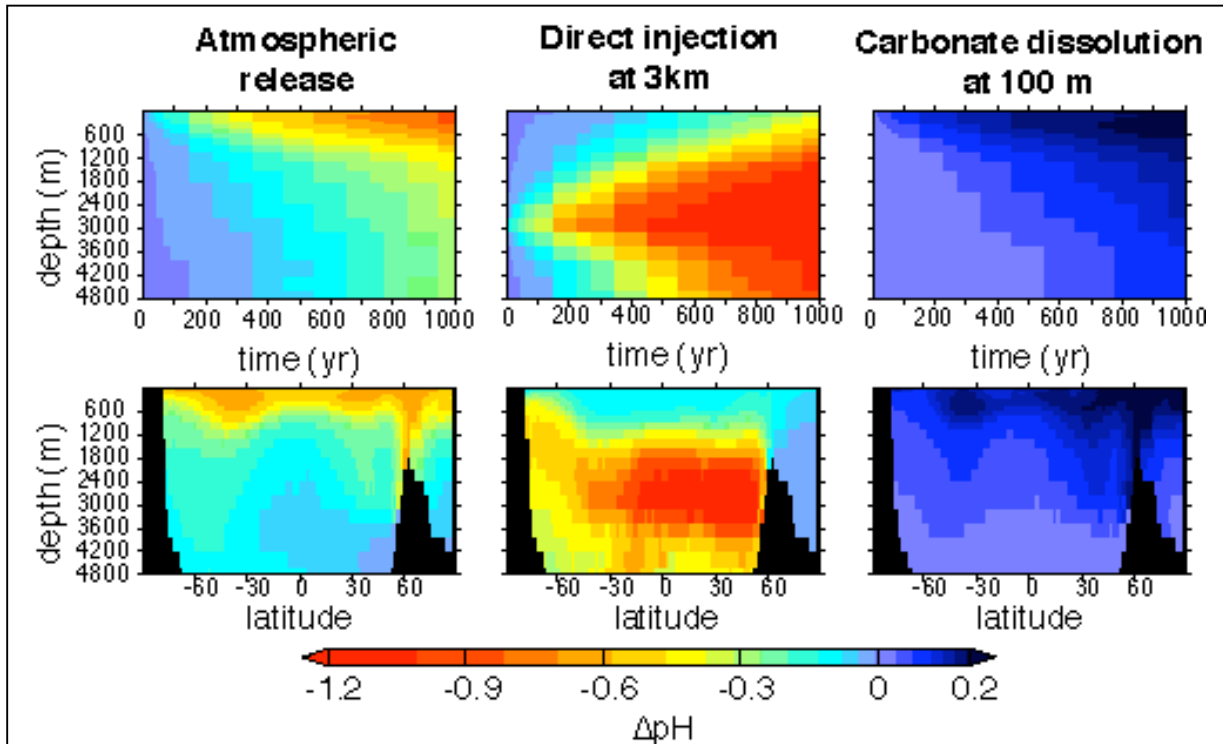


Figure 4. Comparison of ocean GCM simulations of ocean pH changes for atmospheric CO_2 release, direct CO_2 injection at 3 km, and carbonate dissolution at 100m. All releases are 7 GtC of fossil fuel CO_2 per year sustained for 1000 years. The top row shows horizontal mean values as a function of time. The bottom row shows zonal mean values at 500 years of simulation. Atmospheric release decreases ocean pH. Direct injection has a greater impact on deep ocean pH, but diminishes the impact on the surface ocean [and greatly reduces the atmospheric CO_2 burden]. Carbonate dissolution [using the “theoretical maximum” solution from Fig. 1] keeps the CO_2 in the ocean and slightly increases ocean pH, counteracting some of the negative effects of atmospheric release. We need to examine how the chemistry of the “real” process (i.e., not idealized effluents) will (1) be retained in the ocean and affect large-scale ocean pH, and (2) affect ocean chemistry near the point of injection.

mitigation cost offered by accelerated carbonate dissolution would be \$3 - \$4/tonne CO₂ based on previous cost analyses [5,11]. This would especially pertain if the hundreds of millions of gallons of seawater already pumped and used for cooling by these plants each day were subsequently used as a “free” accelerated carbonate dissolution water source.

The preceding baseline CO₂ capture and sequestration cost would significantly out-compete most other current or proposed abiotic technologies and is near DOE’s target of \$2.73/tonne CO₂ mitigated [4]. However, the number of ideal sites and hence the volume of CO₂ that could be treated at this very attractive cost would be small. What cost might be attainable in the more numerous but less favorable settings?

Again assuming free access to seawater and free limestone, the transportation cost of limestone using various modes is listed in Table 1. Assuming a base capital, operating, and maintenance (COM) cost of \$4/tonne CO₂ mitigated, and with carbonate supplied via 2.5 tonnes of low-grade limestone (92% CaCO₃), a limestone transport distance of 200 km yields an accelerated carbonate dissolution CO₂ mitigation cost of about \$6, \$9, \$21, or \$48 per tonne CO₂ using freighter, barge, train, or truck transportation, respectively (Table 1). If limestone must first be purchased at a typical market price of \$5/tonne, this adds \$12.50 to each of the preceding calculations, with the resulting mitigation cost ranging from \$18 to \$61 per tonne CO₂ using the preceding transportation modes. In turn, if fresh seawater rather than recycled cooling water must be used and pumped 2 vertical meters the cost increases to \$23 to \$66/tonne CO₂ (Table 1). By these calculations it is seen that in all but the least ideal cases accelerated carbonate dissolution can be cost-competitive with other forms of CO₂ capture and sequestration, and is often below the cost of amine CO₂ capture alone (generally >\$30/tonne CO₂ [18]). accelerated carbonate dissolution will clearly be more economical under circumstances where limestone and water are low-cost and close at hand.

Alternative Reactor Sitings

The preceding assumes an accelerated carbonate dissolution reactor sited at the source of waste CO₂ (i.e. a power plant) and to which limestone and seawater are transported. While close reactor proximity to the ocean would seem required both to supply water and to dispose of the waste solution, this would not preclude the treatment of waste CO₂ produced inland and transported to coastal accelerated carbonate dissolution reactors sited at or near limestone quarries. Transport of CO₂ is inexpensive (\$0.06 tonne⁻¹ km⁻¹ [19]) relative to the cost of transporting the accelerated carbonate dissolution equivalent (2.5 tonnes) of limestone (Table 1). However, such CO₂ transport requires initial CO₂ separation, capture, and liquefaction, with the associated technology and energy costs that are presently significant, as mentioned above. Still, if inexpensive CO₂ capture/separation is developed, piping CO₂ to coastal accelerated carbonate dissolution reactors could prove cost-competitive with other forms of CO₂ sequestration such as underground storage, especially in regions where the underlying geology is not amenable to CO₂ retention.

Another alternative places accelerated carbonate dissolution reactors on or in seagoing barges or ships that would bring both the limestone and the accelerated carbonate dissolution process to coastal CO₂ point sources accessible by seagoing vessel. In this

way the capital expenditure of an accelerated carbonate dissolution reactor and limestone transport are merged, avoiding potentially costly land-siting of the reactor, and with the ocean readily accessible as a water source and for effluent disposal. This configuration would require that flue gas be piped to and reacted within the docked vessel. Once the ship's supply of limestone had been exhausted by accelerated carbonate dissolution, the ship would be replaced by another loaded vessel/reactor. On its way back to port for limestone reloading, the vessel could dispose of the small amount of unreacted limestone spoils at sea, subject to ocean dumping regulations. The preceding would obviously only be amendable to power plants (or coastal CO₂ sources supplied by pipeline) that are dock-accessible. It also assumes that a limestone-supplying port is within a reasonable shipping distance to the CO₂ source to be mitigated. Rather than the construction and use of new accelerated carbonate dissolution-capable ships, the retrofitting and upgrading of retired or underutilized vessels should be considered as a means of both reducing costs and extending ship utility. Because of their existing hold configuration, freighters and especially tankers would be particularly attractive for such retrofits.

Purpose

The purpose of this project was to develop the scientific information needed evaluate the feasibility of the carbonate-dissolution method for sequestering carbon in the ocean (Rau and Caldeira, 1999; Caldeira and Rau, 2000). Specifically, the primary purposes of this project was to

- (1) demonstrate the carbonate-dissolution approach at bench-top scale,
- (2) evaluate the effectiveness of this approach for storing CO₂ in the ocean, and
- (3) evaluate the effect of the effluent on ocean chemistry.

The purpose of this project is to provide information needed to evaluate whether accelerated carbonate dissolution can play a useful role in carbon management.

Approach

We combined laboratory experiments with modeling, with the laboratory effort focused on demonstrating the carbonate-dissolution approach at bench-top scale (Purpose #1) and the modeling focusing on evaluating the effectiveness and consequences of possible deployment of the carbonate dissolution approach (Purpose #2 and #3).

Laboratory experiments (bench-top scale)

We proposed to demonstrate the carbonate-dissolution technique for sequestration of CO₂ in the ocean at the bench-top scale. We have worked both with fresh water and real seawater, and its much more complicated chemistry. We run a relatively concentrated CO₂ gas stream and water into inert chemical reactors of either mixed or plug flow design containing crushed carbonate of known surface area/volume. We monitor gas and liquid effluent chemistry (including *p*CO₂, pH, conductivity, alkalinity, and metal-ion concentration) to determine dissolution rates and reactor performance under a range of conditions. Questions addressed by the laboratory experiments include: a) impact of flow rate, reactor residence time, bubble size, mixing rate, etc., on the rate of carbonic acid

formation (the rate limiting step being $\text{CO}_2(\text{aq}) \rightarrow \text{H}_2\text{CO}_3$), b) impact of particle size and presence/addition of inhibitors/catalysts on the rate of calcite dissolution, c) impact of acidification, degassing and dilution steps on other seawater solutes, d) maximum degree of supersaturation achievable during partial degassing step prior to carbonate precipitation.

Three-dimensional computer modeling (global scale)

To study the long-term effectiveness of the carbonate-dissolution technique for ocean carbon sequestration, we need to understand the fate of the waste water generated by the process after it is released in the ocean as a function of (1) the chemistry of the effluent, and (2) location and depth of release. Both of these factors will affect the effectiveness of carbonate-dissolution as a carbon sequestration strategy. We have shown the effectiveness of this technique on the global scale using sophisticated ocean circulation and chemistry models available at LLNL.

Technical Accomplishments

We have achieved the primary goals of our study. We have demonstrated that the carbonate dissolution approach works at bench-top scale in the laboratory, and, using models, we have shown that the method can be effective while producing relatively small changes to ocean chemistry. These results have been reported in the following reports.

Documents produced by this project, in full or in part, can be found under the following UCRL numbers:

Report number: UCRL-JC-154438-ABS

Greer, B, Higgins, S R, Eggleston, C M, Boram, L H, Knauss, K G; Study of Heterogeneous Kinetics at Calcite Surfaces in the Presence of Strontium using Atomic Force Microscopy; 2003

Report number: UCRL-JC-153633

Ridgwell, A J, Kennedy, M J, Caldeira, K; Carbonate Deposition, Climate Stability, and Neoproterozoic Ice Ages; 2003

Report number: UCRL-JC-151813-ABS

Caldeira, K; An Overview of Ocean Carbon Storage Options; 2003

Report number: UCRL-JC-151085-ABS

Rau, G H, Caldeira, K; Impacts of CO_2 Storage in the Ocean; 2002

Report number: UCRL-JC-150799-ABS

Rau, G, Caldeira, K; Sequestering CO_2 in the Ocean: Options and Consequences; 2002

Report number: UCRL-JC-149771-ABS

Caldeira, K, Wickett, M E, Rau, G H; Atmospheric CO_2 Concentrations and Ocean pH Impacts Resulting from Atmospheric CO_2 Release, Ocean CO_2 Injection, and Accelerated Carbonate Weathering; 2002

Report number: UCRL-JC-147567-ABS

Caldeira, K, Wickett, M E, Rau, G; Comparing pH Impacts and Ocean CO₂ Storage From Atmospheric CO₂ Release, Oceanic CO₂ Injection, and Injection with Carbonate Dissolution; 2002

Report number: UCRL-JC-144122

Hoffert, M I. Caldeira, K, Benford, G, Criswell, D R, Green, C; Advanced Technology Paths to Global Climate Stability Energy for Greenhouse Planet; 2001

Report number: UCRL-JC-143242-ABS

Rau, G H, Caldeira, K, Downs, B, Sarv, H; Enhanced Carbonate Dissolution as a Means of Capturing and Sequestering Carbon Dioxide; 2001

Report number: UCRL-JC-142499-ABS

Rau, G H, Caldeira, K; Enhanced Carbonate Dissolution as a Means of Sequestering Carbon Dioxide; 2001

Presentations and publications since start of project include

Caldeira, K., M.E. Wickett, and G.H. Rau, *Comparing pH impacts and ocean CO₂ storage from atmospheric CO₂ release, oceanic CO₂ injection, and injection with carbonate dissolution*. Invited talk, **2002 Spring American Geophysical Union Meeting**, May 2002

Rau, G.H., and K. Caldeira, *Minimizing effects of CO₂ storage in the oceans (letter)*. **Science 295, 275-276, 2002**

Rau, G.H., K. Caldeira, and K.G. Knauss. *An effective and less environmentally harmful way to store CO₂ in the ocean*. **2002 AGU Ocean Sciences Meeting**, Feb 2002

Rau, G.H. and K. Caldeira. 1999. Enhanced carbonate dissolution as a means of sequestering carbon dioxide in the ocean. *Transaction, American Geophysical Union* 80(49): 213.

Caldeira, K. and G.H. Rau. 2000. Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. *Geophysical Research Letters* 27: 225-228.

Rau, G.H., and Ken Caldeira. 2000. Enhanced carbonate dissolution as a means of sequestering carbon dioxide in the ocean. *Transactions, American Geophysical Union* 80:OS213.

Rau, G.H., Bill Downs, Ken Caldeira, and Hamid Sarv. 2000. Enhanced carbonate dissolution as a means of sequestering carbon dioxide in the ocean. *Transactions, American Geophysical Union* 81:F283.

Rau, G.H., Ken Caldeira, Kevin G. Knauss, Bill Downs, and Hamid Sarv. 2001. Enhanced carbonate dissolution as a means of capturing and sequestering carbon dioxide. *First National Conference on Carbon Sequestration, Washington D.C., May 14-17, 2001*

Rau, G.H., K.G. Knauss and K. Caldeira. 2001. Enhanced carbonate weathering: helping nature capture and sequester carbon dioxide. Transactions, American Geophysical Union 82:F18.

Rau, G.H., K. Caldeira, and K.G. Knauss. 2002. An effective and less environmentally harmful way to store CO₂ in the ocean. Transaction, American Geophysical Union OS Meeting abstract 51F-05.

Rau, G.H., and Ken Caldeira. 2002. Minimizing effects of CO₂ storage in the oceans. Science 295:275-276.

Ken Caldeira¹, Michael E. Wickett¹, Greg H. Rau, Comparing pH impacts and ocean CO₂ storage from atmospheric CO₂ release, oceanic CO₂ injection, and injection with carbonate dissolution. Transaction, American Geophysical Union OS Meeting in press

Rau, G.H., K.G. Knauss, and K. Caldeira. *Enhanced carbonate weathering: helping nature capture and sequester carbon dioxide*. **2001 Fall American Geophysical Union Meeting**, Dec 2001

Rau, G.H., K. Caldeira, K.G. Knauss, B. Downs, and H. Sarv. Enhanced carbonate dissolution as a means of capturing and sequestering carbon dioxide. **First National Conference on Carbon Sequestration**, May 2001

Summary of technical accomplishments

Following earlier descriptions, the use and impacts of accelerated weathering of limestone (accelerated carbonate dissolution; reaction: $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2(\text{HCO}_3^-)$) as a CO₂ capture and sequestration method is further explored. Since ready access to the ocean is likely an essential requirement for accelerated carbonate dissolution, it is shown that significant limestone resources are relatively close to a majority of CO₂-emitting power plants along the coastal US. Furthermore, waste fines, representing more than 20% of current US crushed limestone production ($>10^9$ tonnes/yr), could be used in many instances as an inexpensive or free source of accelerated carbonate dissolution carbonate. With limestone transportation to coastal sites then as the dominant cost variable, CO₂ sequestration (plus capture) costs of \$3-\$4/tonne are achievable in certain locations. While there is vastly more limestone and water on earth than that required for accelerated carbonate dissolution to capture and sequester all fossil fuel CO₂ production, the transportation cost of bringing limestone, seawater, and waste CO₂ into contact likely limits the method's applicability to perhaps 10-20% of US point-source emissions.

Using a bench-scale laboratory reactor, we show that CO₂ sequestration rates of 10^{-6} to 10^{-5} moles/sec per m² of limestone surface area are readily achievable using seawater. This translates into reaction densities as high as 2×10^{-2} tonnes CO₂ m⁻³ day⁻¹, highly dependent on limestone particle size, solution turbulence and flow, and CO₂ concentration. Our modeling of accelerated carbonate dissolution end-solution disposal in the ocean shows significantly reduced effects on ocean pH and carbonate chemistry relative to those caused by direct CO₂ disposal into the atmosphere or ocean. In fact the increase in ocean Ca²⁺ and bicarbonate offered by accelerated carbonate dissolution

should significantly enhance the growth of corals and other marine calcifiers whose health is currently being threatened by anthropogenic CO₂ invasion and pH reduction in the ocean.

Reaction Rates and Densities

The rate at which reaction 1 occurs (on a per unit limestone surface area per unit time basis) determines the amount of carbonate surface area and time needed to transform a given quantity of CO₂ to HCO₃⁻. In turn, specifying a surface area per volume (A/V) of the carbonate particles determines the basic size of the reactor required for a given CO₂ conversion rate. While previous estimates of these parameters have been made [5], the reaction rates used were based for the most part on idealized dissolution experiments using pure calcite mineral in distilled water under conditions where the diffusional boundary layer around the mineral surfaces were greatly diminished (via stirring). To provide a more realistic assessment of the reaction rate of impure limestone, an experimental, 370 ml (internal volume) bench-scale reactor was used to measure the dissolution rate of limestone in either distilled H₂O or seawater equilibrated with various %CO₂ air streams, and with various water flushing rates, and internal stirring rates (see Figure 1 legend). The results of these experiments yielded dissolution rates ranging from roughly 10⁻⁷ to 10⁻⁵ mols m⁻² s⁻¹ with positive sensitivity to flow rate, stir rate, and CO₂ concentration (Fig. 5). Dissolution rates in seawater were equal to or higher than those in distilled water under otherwise identical conditions (Fig. 1), i.e., the impurities in seawater do not significantly diminish the accelerated carbonate dissolution reaction rate.

Assuming the conditions and results of the 15% CO₂, low-stir-rate and low-flow rate treatments would be characteristic of a large-scale reactor, a reaction rate of about 10⁻⁶ mols m⁻² s⁻¹ is implied (Fig. 1). A limestone particle diameter of 1mm

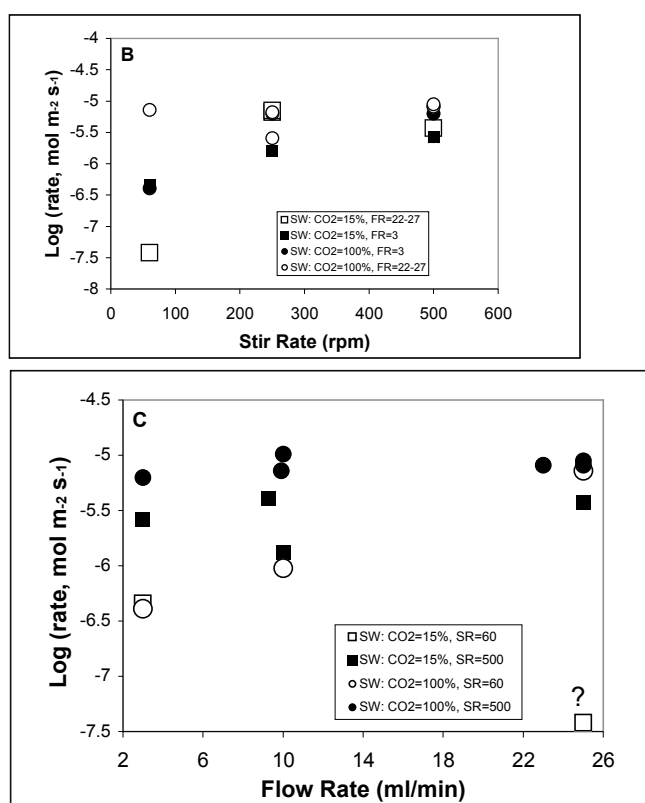


Figure 5. Conversion rate of CO₂ to HCO₃⁻ in an experimental carbonate dissolution reactor flushed with distilled water (DW) or seawater (SW) equilibrated with the % CO₂ shown, and at the various reactor solution flow rates (FR) and internal stir rates (SR) indicated. Stir rates are in revolutions per minute. Conversion rate = ([Ca]_{out} - [Ca]_{in}) x FR / area, where [Ca] refers to the concentration of Ca²⁺ in the solutions entering or

(within the range typical of waste limestone fines discussed above) yields an A/V of $4.4 \times 10^3 \text{ m}^2/\text{m}^3$ or higher depending on the deviation of true particle shape from that of a sphere. Therefore a maximum of 60 m^3 of such limestone particles would be needed to react 1 tonne of CO_2 per day. For a cubic reactor volume (roughly $4\text{m} \times 4\text{m} \times 4\text{m}$), this equates to an areal reaction rate of at least $15 \text{ tonnes CO}_2 \text{ m}^{-2} \text{ day}^{-1}$, or about one million times greater than optimum CO_2 uptake and sequestration rates in managed forests or algal ponds [19]. The experiments show that this density of CO_2 conversion to

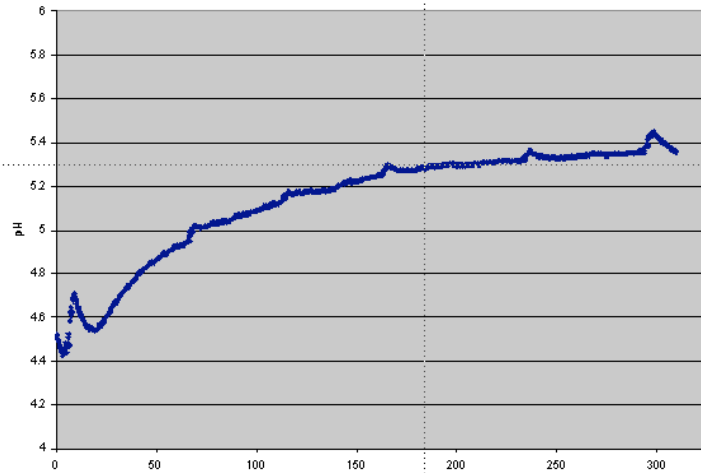


Figure 6. pH as a function of time measured by the instrument shown in Figure 1. The figure shows pH increase as protons attack the limestone mineral surface, buffering carbon acidity.

HCO_3^- could be enhanced by increasing reactor solution stirring and flushing rate. This could be achieved in a full-scale reactor by vigorous bubbling of flue gas within the reactor or by actively recirculating the partially-reacted solution, but with added energy and cost penalties.

Base on the above rates, reaction densities on the order of $10^{-2} \text{ tonnes CO}_2 \text{ m}^{-3} \text{ day}^{-1}$ appear attainable. This means a 20% reduction of the CO_2 emissions from a typical 500MW coal-fired power plant ($10^4 \text{ tonnes CO}_2/\text{day} \times 0.2 = 2 \times 10^3 \text{ tonnes CO}_2/\text{day}$) would require an accelerated carbonate dissolution reactor volume of $2 \times 10^5 \text{ m}^3$, roughly equivalent to a 60m cube. The reactor size required for a given CO_2 mitigation will be highly dependent on limestone particle size, water/gas/solids contacting efficiency, and CO_2 concentration, as well as the purity of the limestone. However, while particle size reduction will theoretically increase limestone surface area and hence reaction density within a reactor, water space between particles and hence flow resistance and contacting efficiency will be reduced. Further research and experimentation is needed in order to determine how to optimize accelerated carbonate dissolution reactor designs for the best cost/benefit.

Effectiveness

Using box models of ocean chemistry and transport Caldeira and Rau [6] showed that the release of the bicarbonate-charged effluent from carbonate dissolution would more effectively sequester CO_2 over the long term relative to direct CO_2 injection at equivalent ocean depths. This has been subsequently confirmed for releases at several different ocean locations and depths in a 3-D ocean general circulation model (e.g., Fig. 4). Injection of pure CO_2 at great depth in the ocean effectively stores most of the injected carbon for hundreds of years or more [6]. Therefore, the additional slowing of CO_2 leakage that would be gained by releasing carbonate dissolution effluent at the same depth may not be

economically significant. Nevertheless, we note that carbonate dissolution can make a major contribution for less costly shallow-water releases and greatly improves effectiveness of long-term ocean carbon sequestration regardless of the depth at which the effluent is released (Fig. 3).

Environmental Impacts/Benefits

An increase in ocean acidity (reduction in pH) is a serious environmental issue caused either by the ongoing diffusive uptake of anthropogenic CO₂ from the atmosphere or the proposed purposeful injection of CO₂ into the ocean (e.g., [10]). Storing waste CO₂ in the form of bicarbonate balanced by calcium ions rather than as dissolved CO₂ (i.e., carbonic acid; bicarbonate balanced by H⁺) substantially lessens the increase in acidity per tone of carbon added to the ocean (Figs. 3,4), while reducing harmful effects to marine biota of direct ocean CO₂ additions [20,21,22]. In fact the addition of bicarbonate-rich effluent to the ocean would be environmentally beneficial in that it would counteract the ongoing reduction of ocean pH, alkalinity, and hence biological calcification rates and productivity [23,24]. Indeed, addition of calcium and/or bicarbonate ions to seawater has been shown to significantly enhance the calcification and growth rate of marine corals (e.g., [25,26,27]). We also point out that accelerated

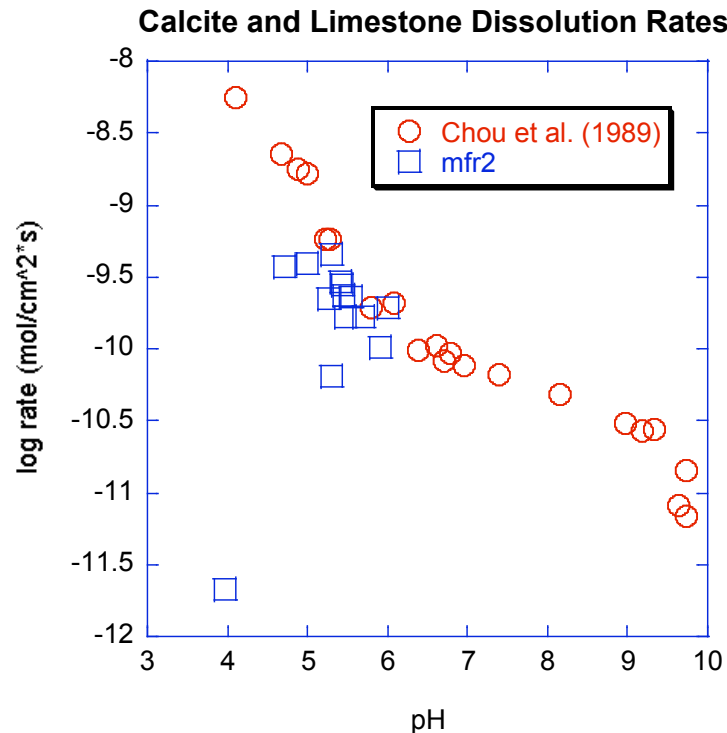


Figure 7. Representation of data on carbonate mineral dissolution from the literature (red circles) and from our experimental apparatus (blue squares). Carbonate dissolution rates in deionized water were determined under a wide range in reactor conditions, using CO₂ streams of 15% and 100%. The two conditions that are clear outliers (falling away from the intrinsic rate data, in spite of being grossly undersaturated with respect to the bulk fluid) represent the extreme minimums of flow rate and stir rate investigated at the two gas concentrations.

carbonate dissolution captures and sequesters CO_2 without the use of any exotic or toxic chemicals, unlike CO_2 capture methods using amines [4].

Nevertheless, negative marine environmental impacts could result downstream from the release of the reactor effluent solution. For example, oxygen concentration would be reduced in the effluent through partial equilibration with flue-gas streams, typically containing only 2-4% O_2 . There may also be impurities released into the effluent solution from the limestone or the flue gas that could be biotically impactful. This could be especially relevant in accelerated carbonate dissolution processing of flue gas from coal-fired power plants, where SO_x , NO_x , trace element, and heavy metal contamination are characteristic. Processing relatively clean flue gas from natural-gas-fired plants or from integrated gasification combine cycle generators would be advantageous in this regard. To our knowledge no previous studies have investigated the marine impacts of effluent streams like those that would emanate from accelerated carbonate dissolution. New, direct experimentation will be required to quantify such effects. We point out, however, that the ocean naturally receives and accommodates about 2×10^9 tonnes of dissolved calcium bicarbonate per year produced from continental carbonate weathering as delivered by rivers [12].

With regard to environmental effects of accelerated carbonate dissolution on land, the current production of crushed stone creates environmental impacts, and these need to be considered for accelerated carbonate dissolution. These impacts include dust and noise generated in mining and processing, but these are relatively benign and confined to the area at or very near the quarries.

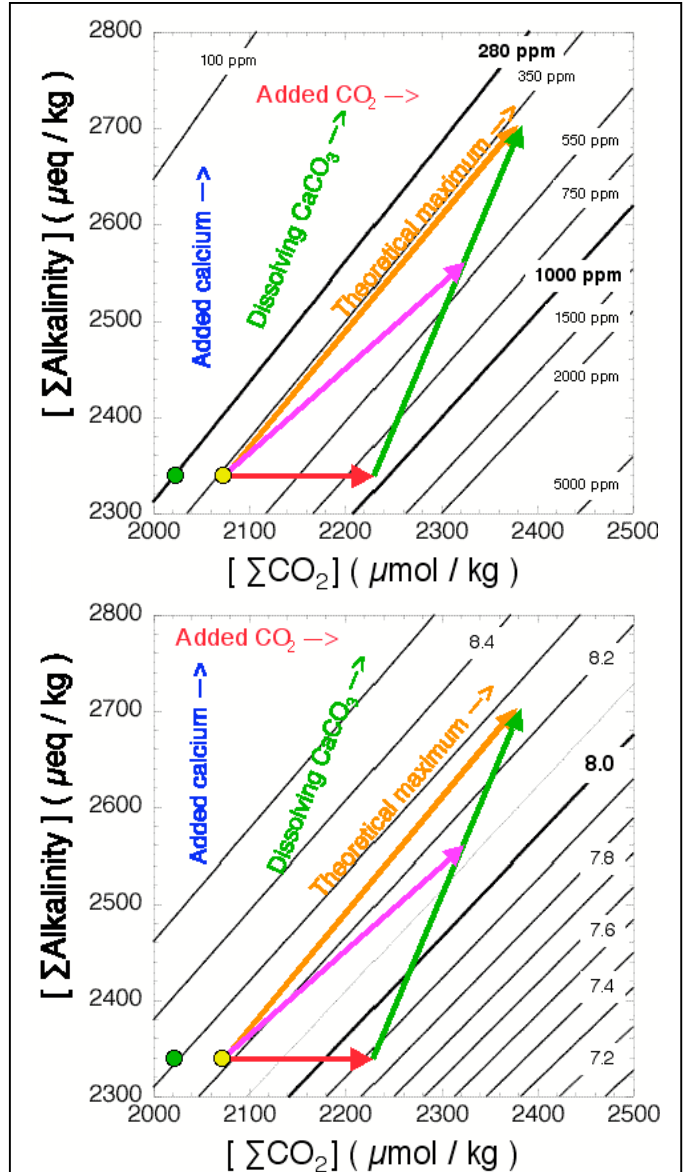


Figure 8. Schematic representation of the carbonate dissolution method of carbon separation and sequestration. Top panel represents pCO_2 , bottom panel represents pH . The orange line represents the theoretical maximum effectiveness for the carbonate dissolution method. The red line represents pure CO_2 injection with no carbonate dissolution. Engineering, cost, and environmental analysis is required to determine the preferred injection composition (magenta line).

Most impacts can be controlled or kept within permissible limits through careful quarry planning and by employing best management practices. However, poorly designed or careless operated quarries, especially in areas of active karst (which occurs in some carbonate rock terrains), have the potential to create far-reaching, serious environmental impacts including lowering of the water table, changing surface- and ground-water flow, pollution of ground water, and sinkhole collapse [28].

The increased transportation of limestone required for accelerated carbonate dissolution would also generate dust and noise en route and during off-loading, and depending on the magnitude of accelerated carbonate dissolution deployment, could significantly tax the existing transportation infrastructure. Additionally, because some fraction of the limestone will not be reacted or reactible, perhaps 5-10% of the original limestone mass transported to accelerated carbonate dissolution reactors would ultimately need to be removed and transported to appropriate waste sites. In addition to ocean disposal of the solid waste (mentioned above), disposal might be performed by loading this waste onto the otherwise empty, overland transports that return to the limestone source, wherein the waste could be used to fill in the original limestone mining excavations. This would make efficient use of the transportation stream and would help reclaim unsightly mining impacts while avoiding the need for new waste sites.

In summary, some environmental effects would result from limestone mining and transportation, but we point out that large-scale mineral extraction and transport is currently an integral part of energy production (e.g., coal, natural gas). We also note that limestone is already used on a large scale for environmental benefit, flue gas desulfurization [29] and acid mine waste neutralization [30] being prime examples. While the benefits of accelerated carbonate dissolution would appear to outweigh whatever environmental and societal impacts might accrue, further assessment of this technology's terrestrial, marine, and human effects is required.

Conclusions

In the appropriate settings accelerated carbonate dissolution is an attractive option for CO₂ mitigation because: 1) the required reactants are relatively inexpensive, abundant, and environmentally benign, 2) the technology is relatively simple, low-cost, and amenable to power plant retrofitting, even in developing countries, 3) the storage is effective and long-term, and 4) the waste products are stable and may have net positive environmental effects for marine life. All of these features derive from the fact that accelerated carbonate dissolution merely enhances Nature's own CO₂ mitigation mechanism, carbonate weathering. More research is needed, however, to more accurately assess the costs, benefits, and impacts of this means of reducing the carbon intensity of global power generation.

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